

WHAT IS CLAIMED IS:

1. A process for creating a carbon-carbon bond by coupling a transferable group to an acceptor group comprising the stages of:

- 5 a) activation of a siliceous compound carrying a group which can be transferred by an activating agent;
- b) addition of a derivative carrying an acceptor group and, simultaneously or consecutively, in any
- 10 order,
- c) addition of a compound of palladacycle type which acts as catalyst of the reaction of coupling the transferable group to the acceptor group by creation of said carbon-carbon bond.

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2. The process as claimed in claim 1, in which the activating agent is an anionic nucleophilic compound selected from hydroxides of alkali metals and alkaline earth metals, alkoxides, carbonates, amides and their

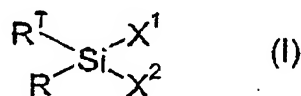
20 derivatives.

3. The process as claimed in claim 2, in which the activating agent is selected from sodium hydroxide, lithium hydroxide, potassium hydroxide, barium

25 hydroxide, barium oxide and the potassium salt of hexamethyldisilazane.

4. The process as claimed in any one of the preceding claims, in which the siliceous compound carrying a transferable group is a dihalosilane

30 corresponding to the formula (I):



in which:

- X^1 and X^2 , which are identical or different,
- 35 are, independently of one another, a halogen atom

selected from fluorine, chlorine, bromine and iodine, preferably from chlorine and bromine; more preferably, X^1 and X^2 are identical and are each a bromine atom or a chlorine atom, advantageously a chlorine atom;

5 • R is selected from the hydrogen atom, the R^T radical defined above and a linear or branched alkyl radical comprising from 1 to 6 carbon atoms, for example selected from methyl, ethyl, propyl, isopropyl, butyl, tert-butyl, sec-butyl, isobutyl, pentyl, 10 neopentyl and n-hexyl, preferably from methyl and ethyl; advantageously, R represents the hydrogen atom, the phenyl radical or the methyl radical;

 • R^T is the transferable group and is selected from an aryl, vinyl and allyl radical, it being 15 possible for each of them optionally to be substituted, R^T preferably representing an optionally substituted aryl radical, for example an optionally substituted phenyl radical.

20 5. The process as claimed in claim 4, in which the dihalosilane carrying a transferable group of formula (I) has the following characteristics, taken in isolation or in combination:

 • X^1 and X^2 are identical and are each a bromine 25 atom or a chlorine atom, advantageously a chlorine atom;

 • R is chosen from the hydrogen atom, the R^T radical defined below and a linear or branched alkyl radical comprising from 1 to 6 carbon atoms, preferably 30 the methyl, ethyl, propyl, isopropyl, butyl, tert-butyl, sec-butyl, isobutyl, pentyl, neopentyl and n-hexyl radical, more preferably the methyl or ethyl radical;

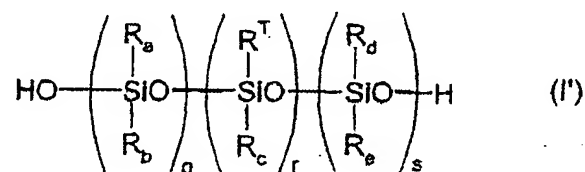
 • R^T is an optionally substituted aryl radical, 35 for example an optionally substituted phenyl radical.

6. The process as claimed in claim 4 or claim 5, in which the dihalosilane of formula (I) is chosen from chlorosilanes.

7. The process as claimed in claim 6, in which the dihalosilane of formula (I) is diphenyldichlorosilane, methylphenyldichlorosilane or methyltolylchlorosilane.

8. The process as claimed in any one of claims 1 to 3, in which the siliceous compound carrying a transferable group is a silicone oil.

9. The process as claimed in claim 8, in which the silicone oil is a polysiloxane of formula (I'):



in which:

15 R^T is a transferable group as defined in claim 4 or claim 5;

20 R_a , R_b , R_c , R_d and R_e , which are identical or different, are selected, independently of one another, from the hydrogen atom, a linear or branched alkyl radical comprising from 1 to 6 carbon atoms and the R^T radical defined above;

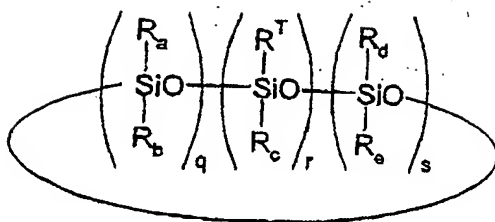
r is an integer between 1 and 10, limits included;

q is 0 or an integer between 1 and 9, limits included; and

25 s is 0 or an integer between 1 and 9, limits included,

the sum $q + r + s$ being between 4 and 10, limits included.

30 10. The process as claimed in claim 9, in which the polysiloxane is in the cyclic form:



11. The process as claimed in any one of the preceding claims, in which the compound carrying an
5 acceptor group corresponds to the formula (II):

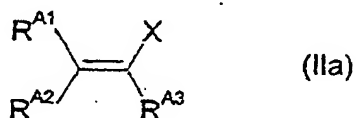


in which:

R^A is a hydrocarbon group (acceptor group)
10 comprising from 2 to 20 carbon atoms and has a double bond situated in the α position with respect to a leaving group X or a monocyclic or polycyclic, aromatic, carbocyclic and/or heterocyclic group;

X is a leaving group, preferably a halogen atom
15 or a sulfonic ester group of formula $-OSO_2-R'$, in which R' is a hydrocarbon group.

12. The process as claimed in claim 11, in which the compound carrying an acceptor group corresponds to
20 the formula (IIa):



in which:

R^{A1} , R^{A2} and R^{A3} , which are identical or
25 different, are selected, independently of one another, from the hydrogen atom and a hydrocarbon group having from 1 to 20 carbon atoms which can be a saturated or unsaturated and linear or branched aliphatic group; a saturated, unsaturated or aromatic, monocyclic or
30 polycyclic, carbocyclic or heterocyclic group; or a

sequence of aliphatic and/or carbocyclic and/or heterocyclic groups;

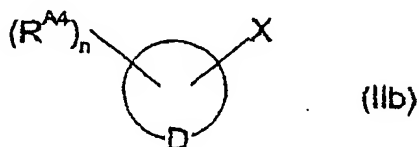
X symbolizes the leaving group as defined in claim 11.

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13. The process as claimed in claim 12, in which the compound carrying an acceptor group is selected from vinyl chloride, vinyl bromide, β -bromostyrene and β -chlorostyrene.

10

14. The process as claimed in claim 11, in which the compound carrying an acceptor group corresponds to the formula (IIb):



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in which:

D symbolizes the residue of a ring forming all or part of a monocyclic or polycyclic, aromatic, carbocyclic and/or heterocyclic system,

X is a leaving group as defined in claim 5,

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R^{A4} , which are identical or different, are substituents on the ring,

n is the number of substituents on the ring.

15. The process as claimed in claim 14, in which
25 the compound carrying an acceptor group corresponds to the formula (IIb) where D is the residue of a cyclic compound which preferably has at least 4 atoms in the ring, preferably 5 or 6, which is optionally substituted and which represents at least one of the
30 following rings:

* a monocyclic aromatic carbocycle or a polycyclic aromatic carbocycle, that is to say a compound composed of at least 2 aromatic carbocycles which form, between them, ortho- or ortho- and peri-

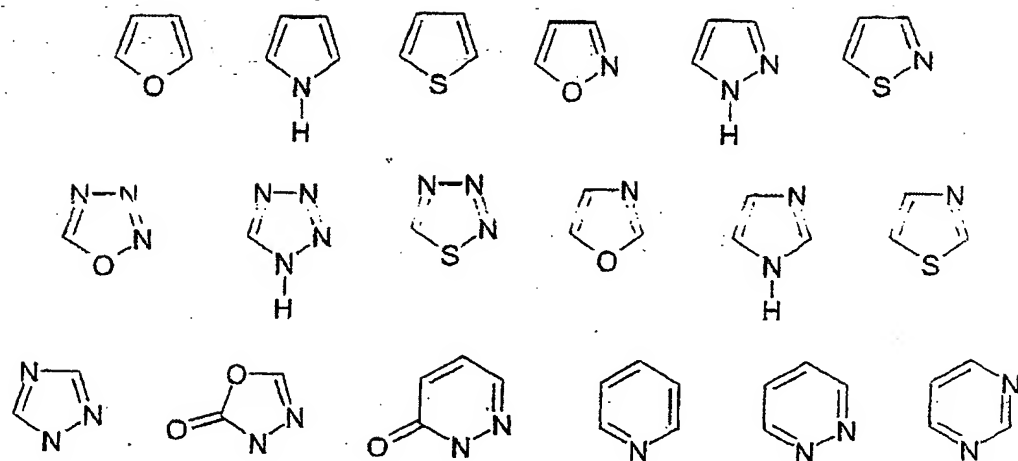
fused systems or a compound composed of at least 2 carbocycles, of which one alone of them is aromatic, which form, between them, ortho- or ortho- and peri-fused systems;

- 5 * a monocyclic aromatic heterocycle comprising at least one of the heteroatoms chosen from oxygen, nitrogen and sulfur or a polycyclic aromatic heterocycle, that is to say a compound composed of at least 2 heterocycles comprising at least one heteroatom
10 in each ring, at least one of the two rings of which is aromatic, which form, between them, ortho- or ortho- and peri-fused systems, or a compound composed of at least one carbocycle and at least one heterocycle, at least one of the rings of which is aromatic, which
15 form, between them, ortho- or ortho- and peri-fused systems.

16. The process as claimed in claim 15, in which the compound carrying an acceptor group corresponds to
20 the formula (IIb) where D is the residue of an optionally substituted aromatic carbocycle, such as benzene, of an aromatic bicycle comprising two aromatic carbocycles, such as naphthalene, or of a partially aromatic bicycle comprising two carbocycles, one of the
25 two of which is aromatic, such as 1,2,3,4-tetrahydronaphthalene.

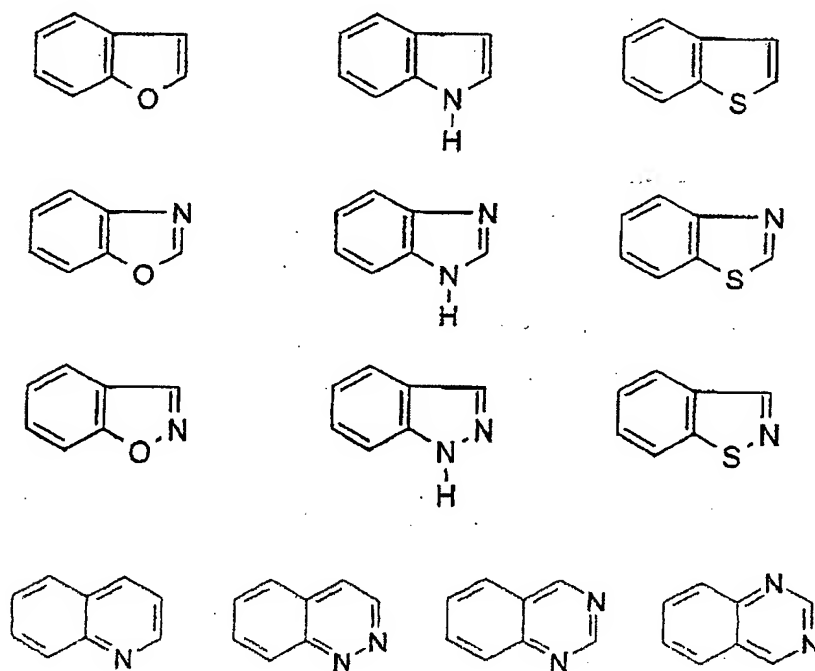
17. The process as claimed in claim 15, in which the compound carrying an acceptor group corresponds to
30 the formula (IIb) where D is the residue of a heterocycle chosen from:

- an aromatic heterocycle:



- an aromatic bicycle comprising an aromatic carbocycle and an aromatic heterocycle:

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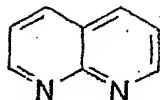


- a partially aromatic bicycle comprising an aromatic carbocycle and a heterocycle:

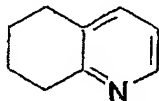


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- an aromatic bicycle comprising two aromatic heterocycles:

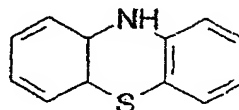
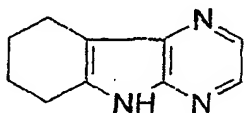


- a partially aromatic bicycle comprising a carbocycle and an aromatic heterocycle:



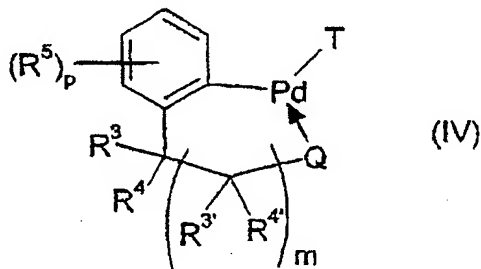
, and

5 - a tricycle comprising at least one carbocycle or one heterocycle which is aromatic:



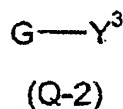
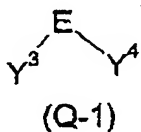
18. The process as claimed in any one of the preceding claims, in which the compound carrying an acceptor group is selected from p-chlorotoluene, p-bromoanisole and p-bromotrifluoromethylbenzene.

19. The process as claimed in any one of the preceding claims, in which the palladacycle compound corresponds to the following formula (IV):



in which:

* Q is a group of formula (Q-1) or a group of formula (Q-2):



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in which groups:

- E is selected from the nitrogen, phosphorus or arsenic atom;

- G is selected from the sulfur, oxygen, selenium and carbon atom; and

5 - Y^3 and Y^4 , which are identical or different, are selected from:

10 . a linear or branched alkyl radical having 1 to 16 carbon atoms which is optionally substituted by one or more phenyl, hydroxyl, halogen, nitro, alkoxy or alkoxycarbonyl groups or atoms, the alkoxy groups having 1 to 4 carbon atoms;

15 . a linear or branched alkenyl radical having 2 to 12 carbon atoms;

20 . an aryl radical having 6 to 10 carbon atoms which is optionally substituted by one or more alkyl groups having 1 to 4 carbon atoms, alkoxy or alkoxycarbonyl groups, the alkoxy radical having 1 to 4 carbon atoms, or halogen atoms;

25 . it being possible for Y^3 to Y^4 and together to form a linear or branched alkylene, alkenylene or alkadienylene radical having from 3 to 6 carbon atoms;

30 . it being possible for Y^3 or Y^4 to form, with R^4 or $R^{4'}$ and with the atoms to which they are connected, an unsaturated or completely or partially unsaturated 5- or 6-membered ring;

35 . it additionally being possible for one of Y^3 or Y^4 to be hydrogen, the other being as defined above;

 - it additionally being possible for Y^3 to form a bond with R^3 (or $R^{3'}$) when E is the nitrogen atom and, in this case, Y^4 can also be the hydroxyl group;

* T is a counterion commonly understood as such by a person skilled in the art and is generally selected from the anions of the following groups: -F, -Cl, -Br,

-I, -CN, -OCN, -SCN, -CF₃, -OCF₃, -SCF₃, -ONO, -ONO₂,
-OSO₂N(R⁶)(R⁷), -SO₂R⁸, -OSO₂R⁸, -O(O)CR⁸, -SR⁸, -N₃ and
-OR⁸;

* R³, R⁴, R^{3'} and R^{4'}, which are identical or
5 different, are selected from the hydrogen atom and a
linear or branched alkyl radical comprising from 1 to 6
carbon atoms; preferably, R³, R⁴, R^{3'} and R^{4'}, which are
identical or different, are the hydrogen atom or the
methyl radical, more preferably the hydrogen atom; it
10 additionally being possible for R³, R⁴, R^{3'} or R^{4'} to
form, with Y³ and/or Y⁴ and/or R⁵, together with the
atoms to which they are connected, an unsaturated or
completely or partially unsaturated 5- or 6-membered
ring;

15 * R⁵, which are identical or different, are
substituents on the ring, preferably one of the groups
selected from the linear or branched alkyl group having
from 1 to 6 carbon atoms, preferably from 1 to 4 carbon
atoms, such as methyl, ethyl, propyl, isopropyl, butyl,
20 isobutyl, sec-butyl or tert-butyl; a linear or branched
alkenyl or alkynyl group having from 2 to 6 carbon
atoms, preferably from 2 to 4 carbon atoms, such as
vinyl or allyl; a linear or branched alkoxy or
thioether group having from 1 to 6 carbon atoms,
25 preferably from 1 to 4 carbon atoms, such as the
methoxy, ethoxy, propoxy, isopropoxy or butoxy groups,
an alkenyloxy group, preferably an allyloxy group, or a
phenoxy group; a cyclohexyl, phenyl or benzyl group; an
acyl group having from 2 to 6 carbon atoms; a group of
30 formula -R¹-OH, -R¹-SH, -R¹-COOR², -R¹-CO-R², -R¹-CHO,
-R¹-CN, -R¹-N(R²)₂, -R¹-CO-N(R²)₂, -R¹-SO₃Z, -R¹-SO₂Z, -R¹-
Y or -R¹-CF₃; in which formulae R¹ is a valency bond or
a saturated or unsaturated, linear or branched,
divalent hydrocarbon group having from 1 to 6 carbon
35 atoms, such as, for example, methylene, ethylene,
propylene, isopropylene or isopropylidene; the R²
groups, which are identical or different, are a
hydrogen atom or a linear or branched alkyl group
having from 1 to 6 carbon atoms or a phenyl group; Z is

a hydrogen atom, an alkali metal, preferably sodium, or an R^2 group; Y symbolizes a halogen atom, preferably a chlorine, bromine, iodine or fluorine atom; R^5 can additionally form, with R^3 , R^4 , $R^{3'}$ or $R^{4'}$, Y^3 , Y^4 or another R^5 substituent, together with the atoms to which they are connected, an unsaturated or completely or partially unsaturated 5- or 6-membered ring;

* R^6 and R^7 , which are identical or different, are the hydrogen atom or a linear or branched C_1 - C_{16} alkyl group;

* R^8 is a linear or branched C_1 - C_{16} alkyl group;

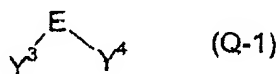
* p is the number of substituents on the ring, that is to say 0, 1, 2, 3 or 4; and

* m is 0 or 1,

it also being possible for the palladacycle of formula (IV) to exist in the dimeric form.

20. The process as claimed in claim 19, in which the palladacycle of formula (IV) has one or more of the following characteristics, taken in isolation or in combination:

* Q is a group of formula (Q-1):



in which:

- E is the nitrogen atom;

- Y^3 and Y^4 , which are identical or different, are a linear or branched alkyl radical having 1 to 16 carbon atoms, preferably from 1 to 6 carbon atoms, more preferably the methyl radical; it additionally being possible for one of Y^3 or Y^4 to be hydrogen, the other being as defined above;

- it additionally being possible for Y^3 to form a bond with R^3 (or $R^{3'}$) when E is the nitrogen atom and, in this case, Y^4 can also be the hydroxyl group;

* T is a halogen, preferably -F, -Cl, -Br or -I, preferably -Cl;

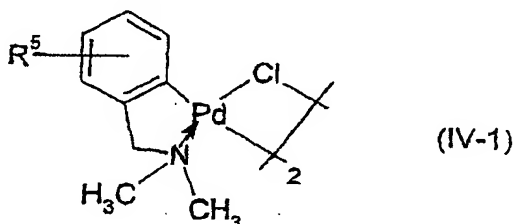
* R^3 , R^4 , $R^{3'}$ and $R^{4'}$, which are identical

different, are the hydrogen atom or the methyl radical, more preferably the hydrogen atom;

* R^5 , which are identical or different, are one of the groups selected from a linear or branched alkyl group having from 1 to 6 carbon atoms, preferably from 1 to 4 carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, *sec*-butyl or *tert*-butyl; or a halogen atom, preferably a chlorine, bromine or fluorine atom;

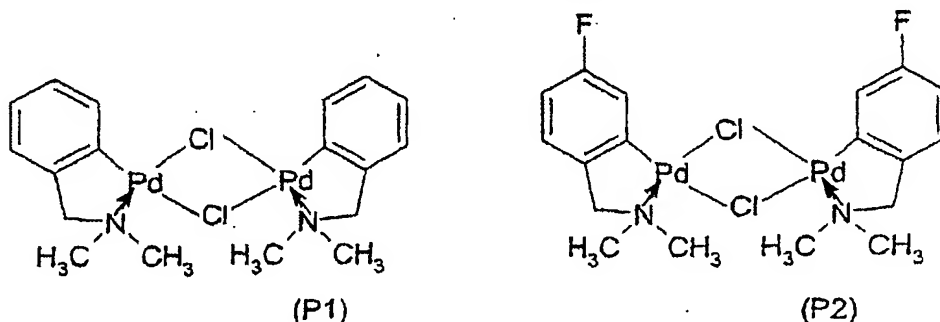
* p is 0, 1 or 2; and
* m is 0.

21. The process as claimed in any one of the preceding claims, in which the palladacycle corresponds to the following formula (IV-1):



in which R^5 is as defined in claim 16, preferably a hydrogen or halogen atom.

22. The process as claimed in any one of the preceding claims, in which the palladacycle is selected from the palladacycle P1 or the palladacycle P2:



23. The process as claimed in any one of the preceding claims, in which the amount of catalyst employed is generally between 0.0005 mol% and 2 mol%, preferably between 0.01 mol% and 1 mol%, in particular

less than 0.1 mol% (1000 ppm), with respect to the compound carrying the acceptor group.

24. The process as claimed in any one of the preceding claims, in which the solvent of stage a) is dioxane or anisole.

25. The process as claimed in one of the preceding claims, additionally comprising, between stage b) and stage c), the addition of a phase transfer agent.

26. The process as claimed in claim 25, in which the phase transfer agent is selected from tetrabutylammonium iodide, tetrabutylammonium chloride, tetrabutylammonium bromide, tetramethylammonium bromide and cetyltrimethylammonium bromide.

27. The process as claimed in any one of the preceding claims, comprising the stages of:

20 a) activation of a dichlorosilane by an alkali metal or alkaline earth metal hydroxide;

b) addition of an aryl halide and of a palladacycle catalyst, optionally in the presence of a phase transfer agent;

25 c) separation and isolation of the product of the coupling reaction.

28. The process as claimed in claim 27, comprising the stages of:

30 a) activation of diphenyldichlorosilane by sodium hydroxide;

b) addition of 4-trifluoromethyl-1-bromobenzene and of palladacycle catalyst P2, in the presence of tetrabutylammonium bromide as phase transfer agent;

35 c) separation and isolation of the product of the coupling reaction, which is [4'-(trifluoromethyl)phenyl]benzene.

29. The process as claimed in claim 27, comprising

the stages of:

a) activation of methylphenyldichlorosilane by sodium hydroxide;

5 b) addition of 4-trifluoromethyl-1-bromobenzene and of palladacycle catalyst P1, in the presence of tetrabutylammonium bromide as phase transfer agent;

c) separation and isolation of the product of the coupling reaction, which is [4'-(trifluoromethyl)phenyl]benzene.

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30. The process as claimed in claim 27, comprising the stages of:

a) activation of methylphenyldichlorosilane by sodium hydroxide;

15 b) addition of 2-methyl-1-bromobenzene and of palladacycle catalyst P1, in the presence of tetrabutylammonium bromide as phase transfer agent;

c) separation and isolation of the product of the coupling reaction, which is (2'-methyl-phenyl)benzene.

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31. The process as claimed in claim 27, comprising the stages of:

25 a) activation of methylphenyldichlorosilane by sodium hydroxide;

b) addition of 4-methoxy-1-bromobenzene and of palladacycle catalyst P1, in the presence of tetrabutylammonium bromide as phase transfer agent;

30 c) separation and isolation of the product of the coupling reaction, which is (4'-methoxy-phenyl)benzene.

32. The process as claimed in one of claims 1-26, comprising the stages of:

35 a) activation of a silicone oil by an alkali metal or alkaline earth metal hydroxide;

b) addition of an aryl halide and of a palladacycle catalyst, optionally in the presence of a phase transfer agent;

c) separation and isolation of the product of the coupling reaction.

33. The process as claimed in claim 32, comprising
5 the stages of:

a) activation of methylphenylpolysiloxane by sodium hydroxide;

b) addition of 4-trifluoromethyl-1-bromobenzene and of palladacycle catalyst P1;

10 c) separation and isolation of the product of the coupling reaction, which is [4'-(trifluoromethyl)phenyl]benzene.

34. The process as claimed in claim 32, comprising
15 the stages of:

a) activation of methylphenylpolysiloxane by sodium hydroxide;

b) addition of 4-methoxy-1-bromobenzene and of palladacycle catalyst P1;

20 c) separation and isolation of the product of the coupling reaction, which is (4'-methoxyphenyl)benzene.